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RADICAL POLYMERIZATION OF STYRENE IN THE PRESENCE OF NITROXYL RADICALS. EXPERIMENTS AND SIMULATIONS.

by

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Polymerization of styrene in the presence of a stable radical TEMPO has been simulated using a Predici simulations package. Based on the experimental data, a kinetic model for the TEMPO-moderated polymerization of styrene has been proposed. It was shown that in order to properly simulate the experimental data, in addition to the reversible cleavage of the TEMPO-polymeric radical adduct, it is necessary to include thermal self-initiation, transfer and irreversible decomposition of intermediate alkoxyamines in the polymerization model. This model, combined with the experimental data and literature values of the rate constants of propagation (k_p), termination (k_t), transfer (k_{trm}), and alkoxyamines decomposition (k_{decomp}), was then employed to estimate kinetic and thermodynamic parameters of the exchange between dormant and active species. The equilibrium constant K was estimated to be around $1 \cdot 10^{-10}$ mol/L, the deactivation rate constant $k_d = 3 \cdot 10^{7} mol^{-1}Ls^{-1}$ and the activation rate constant $k_a = 3 \cdot 10^{-3} mol^{-1}Ls^{-1}$ for bulk styrene polymerization at 120°C.

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Radical Polymerization of Styrene in the Presence of Nitroxyl Radicals. Experiments and Simulations.

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Introduction

Radical polymerization, in spite of its commercial importance, has been very difficult to control at a level attained for anionic and cationic polymerization. A rational design and approach to controlled/living radical polymerization based on the reversible formation of growing radicals from various types of dormant species, has been presented only very recently[1]. Use of a stable radical TEMPO (2,2,6,6,-tetramethyl-1-piperidinyl -oxy) and corresponding alkoxyamines as moderators for radical polymerization of styrenes has been probably most extensively studied[2-7] but the exact mechanism and reasons for the preparation of well defined polymers are still obscure. The objective of this paper is to summarize experimental data obtained in different but comparable systems and provide a comprehensive view on the polymerization of styrene in the presence of TEMPO. By using computer simulations, effects of various reactions occurring in this system, including self-initiation, termination, transfer, decomposition of alkoxy-amines, as well as dynamics of exchange on kinetics, molecular weights and polydispersities are analyzed.

Simulations were performed using program PREDICI which is based on a adaptive Rothe method[8] as a new numerical strategy for time discretization. It uses a discrete Galerkin h-p method to represent chain length distribution and allows to follow concentration of all substrates, low and high molecular weight products and intermediates as well as molecular weights and the corresponding distributions of all types of macromolecules.

Elementary Reactions Involved In TEMPO Mediated Styrene Polymerization

The simplest system for the TEMPO mediated styrene polymerization includes styrene and the corresponding TEMPO adduct, 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine, MT. The basic reactions in such system include:

- **homolytic cleavage of the adduct:**

$$MT \underset{k_d}{\overset{k_a}{\rightleftharpoons}} M^* + T^* \quad (1)$$

- **initiation and subsequent propagation:**

$$M^* + M \xrightarrow{k_p} P_1^* \quad (2)$$

$$P_n^* + M \xrightarrow{k_p} P_{n+1}^* \quad (3)$$

To simplify the analysis it is assumed that $k_{p1}=k_{pn}=k_p$. Values of propagation rate constants are available in literature and they are $k_p=2\cdot10^3$ $mol^{-1}\cdot L\cdot s^{-1}$ at 120°C [9].

- **reversible deactivation of active chains:**

$$P_n^* + T^* \underset{k_a}{\overset{k_d}{\rightleftharpoons}} P_nT \quad (4)$$

- **termination** with a rate constant $k_t=10^7$ $mol^{-1}\cdot L\cdot s^{-1}$ at 120°C [10]

$$P_n^* + P_m^* \xrightarrow{k_t} P_{n+m} \quad (5)$$

- **thermal initiation**, presumably by formation of unsaturated dimers[11]

$$M + M \xrightarrow{k_{dim}} D \quad (6)$$

The rate of thermal formation of dimer has been determined by using various inhibitors. By extrapolation of the data available in literature[12,13] the rate of dimer formation at 120°C was estimated to be approximately $1\cdot10^{-6} mol\cdot L^{-1}$. From this value $k_{dim}=1\cdot10^{-8}$ $mol^{-1}\cdot L\cdot s^{-1}$ was calculated.
The actual initiation probably occurs via hydrogen atom transfer to monomer as shown in Equation7.

$$D + M \xrightarrow{k_i'} D^* + M^* \quad (7)$$

There is no literature data about this step of thermal initiation. In order to fit the experimental kinetic data $k_i'= 3\cdot10^{-8}$ $mol^{-1}\cdot L\cdot s^{-1}$ was used. Additionally it was assumed that the dimer radical D* reacts with monomer with the same rate constant as monomeric radical.

Although the simulations with the model based on equations 1-7 fit the experimental kinetic data very well, the calculated molecular weights were 100 times too high. In order to fit the molecular weights, a transfer to monomer was added to the model. However, it did not result in a significant decrease of molecular weights (at 120 °C $C_{trM}=1.4\cdot10^{-4}$ [14], $k_{trM}=0.28$ $mol^{-1}\cdot L\ s^{-1}$).

$$P_n^* + M \xrightarrow{k_{trm}} P_n + M^* \quad (8)$$

Because most polymerizations were studied only to moderate conversions (<70%), transfer to polymer was not taken into account in these simulation.

When a transfer to the Mayo dimer (Eq.9) was incorporated into the model, a good agreement between observed and calculated molecular weights was obtained. The optimum fit was achieved for $k_{trD}=50$ $mol^{-1}\cdot L\cdot s^{-1}$. This relatively large value is justified as suggested by Olaj and coworkers[15].

$$D + P^*_n \xrightarrow{k_{trD}} D^* + P_n \quad (9)$$

It has been reported that the adduct spontaneously thermally decomposes to styrene and hydroxylamine[16] (Eq.10). Macromolecular species should decompose with the similar rate constant $k_{decomp}= 3\cdot10^{-5}s^{-1}$ at 120 °C (Eq.11).

$$MT \xrightarrow{k_{decomp.}} M^* + TH \quad (10)$$

$$PT \xrightarrow{k_{decomp}} P^= + TH \quad (11)$$

Results and Discussion:

Kinetics of polymerization

Figure 1 illustrates a simulated kinetics of thermal self-initiated polymerization of styrene, together with a simulated kinetics of polymerization in the presence of 2,2,6,6-tetramethyl-1-(1-phenylethoxy) piperidine and with experimental data from literature on polymerization initiated by AIBN or BPO and TEMPO or its adduct at 120 °C.

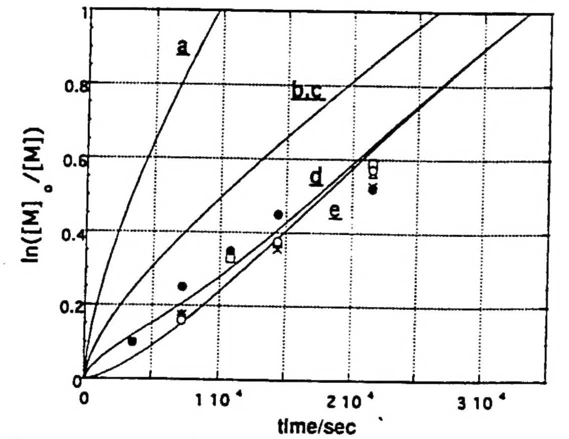

Figure 1. Kinetic plots for the simulated polymerization of styrene in the presence of adduct [0.012M] in bulk at 120°C with variable kinetics and thermodynamics of exchange, simulated thermal polymerization of styrene and experimental data for different adduct concentrations: a: $K=1\cdot10^{-9}$, $k_d=1\cdot10^9$, $k_a=1\cdot10^0$; b: $K=1\cdot10^{-10}$, $k_d=1\cdot10^7$, $k_a=1\cdot10^{-3}$; c: $K=1\cdot10^{-10}$, $k_d=1\cdot10^9$, $k_a=1\cdot10^{-1}$; d: $K=1\cdot10^{-11}$, $k_d=1\cdot10^9$, $k_a=1\cdot10^{-2}$; e: thermal polymerization; exp. data: x [adduct]=0.012M; + [adduct]=0.009M; Δ [adduct]=0.003M[17]; ○ [adduct]=0M; □ [adduct]= 0.010M[18]; ♦ [AIBN]= [TEMPO]=0.010M[5]; ● [BPO]= [TEMPO] =0.010M[3,19]; (K is in mol/L, k_d is in $mol^{-1}\cdot L\cdot s^{-1}$ and k_a in s^{-1})

The best fit to experimental kinetic data, was found for values of the equilibrium constant $K=k_a/k_d\leq10^{-10}$mol/L, preferably $K=10^{-11}$mol/L. Apparently the dynamics of exchange has no effect on kinetics. Using either upper limit of the rate constants of deactivation $k_d=10^9 mol^{-1}\cdot L\cdot s^{-1}$ or 100 times lower values $k_d=10^7 mol^{-1}\cdot L\cdot s^{-1}$ (and correspondingly $k_a=10^{-1}s^{-1}$ and $10^{-3}s^{-1}$) has no effect on the rate of monomer consumption. $K=10^{-10}$ mol/L is the upper limit for the equilibrium constant and lower values such as 10^{-11} mol/L also fit the observed kinetics.

Equilibrium TEMPO concentrations

The available literature data and also estimates by UV and EPR indicate that approximately 1 to 10% of TEMPO (based on the initial alkoxyamine) is formed in the reaction[5,20]. The simulations showed that such high concentration of TEMPO is possible only in a system with the equilibrium constant K not lower than 10^{-10} mol/L at 120°C. Thus taking this into account as well as the results from kinetics simulations, the equilibrium constant K should be ≈10^{-10} mol/L.

Evolution of molecular weights and polydispersities with conversion.

No transfer, no decomposition

Figure 2 illustrates the evolution of molecular weights with conversion for the simplest systems without transfer and decomposition with variable exchange rates but constant value $K=10^{-10}$ mol/L. It seems that some of the reported data agree relatively well with simulations if the rate of activation is larger than $k_a>10^{-3}$ s^{-1} ($k_d>10^7$ $mol^{-1}{\cdot}L{\cdot}s^{-1}$). Too high initial molecular weight are predicted for smaller values of the exchange rate constants.

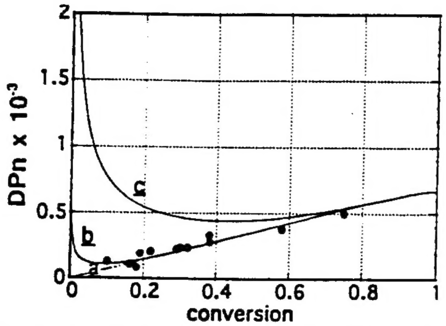

Figure 2. Simulated dependence of number average degree of polymerization on conversion in systems with variable kinetics and equilibrium constant $K=1{\cdot}10^{-10}$mol/L: a: $k_d=1{\cdot}10^9$, $k_a=1{\cdot}10^{-1}$; b: $k_d=1{\cdot}10^8$, $k_a=1{\cdot}10^{-2}$; c: $k_d=1{\cdot}10^7$, $k_a=1{\cdot}10^{-3}$. Solid points correspond to experimental data (c.f. fig.1) (k_d is in $mol^{-1}{\cdot}L{\cdot}s^{-1}$ and k_a in s^{-1})

Figure 3 depicts variation of polydispersities with conversion for various values of rate constants of activation and deactivation. The initial best fit was found for $k_d=3{\cdot}10^7$ $mol^{-1}{\cdot}L{\cdot}s^{-1}$, a value which is substantially lower than the expected diffusion controlled values $k_d \approx 10^9$ $mol^{-1}{\cdot}L{\cdot}s^{-1}$. This can be ascribed either to higher viscosity of the system or to steric effects decreasing the reactivity of a macroradical. In systems with slow exchange a monotonous decrease of polydispersity with conversion is expected. The observed polydispersities increase at higher conversions. Thus some additional side reactions contribute to the broadening of molecular weight distribution.

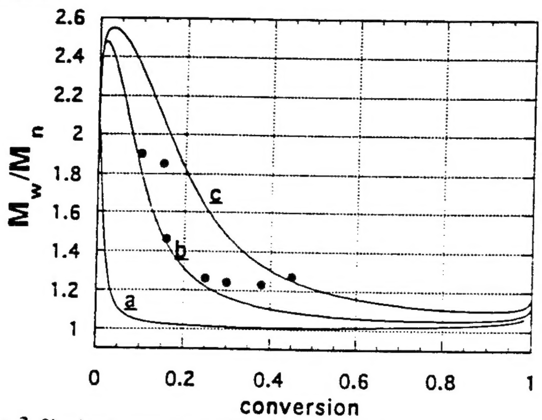

Figure 3. Simulated dependence of molecular weight distributions on conversion in systems with variable kinetics and equilibrium constant $K=1{\cdot}10^{-10}$mol/L: a: $k_d=1{\cdot}10^9$, $k_a=1{\cdot}10^{-1}$; b: $k_d=3{\cdot}10^7$, $k_a=3{\cdot}10^{-3}$; c: $k_d=1{\cdot}10^7$, $k_a=1{\cdot}10^{-3}$ (k_d is in $mol^{-1}{\cdot}L{\cdot}s^{-1}$ and k_a in s^{-1}). Solid points correspond to experimental data (c.f. Fig.1).

Transfer to monomer and decomposition of alkoxyamines

Figure 4 demonstrates the effect of thermal self-initiation, transfer to monomer and decomposition of alkoxyamines on molecular weight distribution. Both self-initiation and transfer lead to relatively small increase of polydispersities, lower than experimentally observed. However, larger, and much closer to those observed experimentally, polydispersities are predicted by taking into account the decomposition reaction (eq. 10 and 11).

In summary, it seems that the values of rates constants used in this work lead to successful simulation of observed rates, molecular weights and polydispersities of obtained of polymers and TEMPO concentrations. Thus, the apparently simple polymerization of styrene moderated by TEMPO adducts includes several other reactions: self-initiation, termination, transfer and decomposition of alkoxyamines.

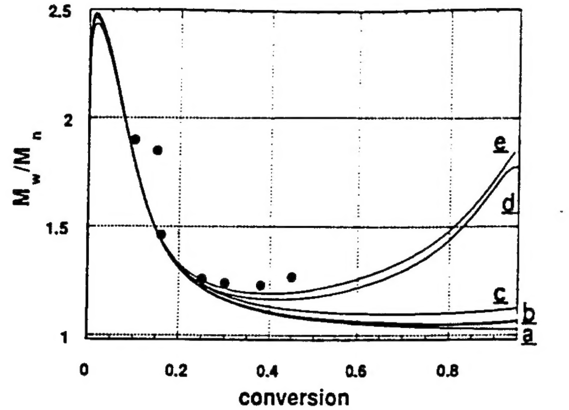

Figure 4. Effect of various side reactions on simulated dependence of molecular weights distributions on conversion in systems with $K=1{\cdot}10^{-10}$mol/L, $k_d=1{\cdot}10^9$$mol^{-1}{\cdot}L{\cdot}s^{-1}$, $k_a=1{\cdot}10^{-1}s^{-1}$; a: exchange only; b: thermal initiation, c: transfer to monomer; d: decomposition of alkoxyamine; e: all side reactions combined. Solid points correspond to experimental data (c.f. Fig.1).

Conclusions

TEMPO moderated polymerization of styrene proceeds with the very low stationary concentration of radicals generated by homolytic cleavage of alkoxyamines. Polymerization rates in the absence and in the presence of variable concentrations of alkoxyamines are nearly the same, indicating that majority of radicals are produced by self initiation. The equilibrium constant of reversible cleavage of alkoxyamines at 120oC is $K \approx 10^{-10}$mol/L as estimated from kinetics and concentration of TEMPO observed in the polymerization. Rate constant of activation (cleavage) of alkoxyamines is in the range of $k_a \approx 3{\cdot}10^{-3}$ s^{-1}. Correspondingly, rate constant of deactivation (reaction of growing radicals with TEMPO) is in the range of $k_d \approx 3{\cdot}10^7$ $mol^{-1}{\cdot}L{\cdot}s^{-1}$. In addition to self-initiation, propagation, exchange and termination, other side reactions such as transfer and decomposition of alkoxyamines are also present.

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